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Electrooxidation of Soluble α,α-Coupled Thiophene Oligomers

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13 ABSTRACT (Maximum 200 words)

The electrooxidation of α,α-coupled thiophene oligomers with terminal trimethylsilyl and β-methyl groups was studied in methylene chloride at room temperature. The oligomers with 4, 5, and 7 thiophene rings undergo two stepwise oxidations to produce the radical cation and dication, respectively, as confirmed by Vis/Nir esr spectra. The redox wave are chemically reversible and are well-separated (ca. 200 mV) in the cyclic voltammagram and suggested that the same electrochemical behavior should be observed with the next higher oligomers or in the π-conjugated segments of polythiophene. Thus the broad featureless voltammagram observed with films of polythiophene is not an inherent property of the polymer segments but may reflect complications from the solid state nature of the film.

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Electrooxidation of Soluble α,α-Coupled Thiophene Oligomers

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Abstract

The electro-oxidation of α-α coupled thiophene oligomers with terminal α-$(CH_3)_3Si$ groups (α-TMS) and β-CH_3 groups were studied in methylene chloride at room temperature. The oligomers with 4, 5 and 7 thiophene rings undergo two stepwise oxidations to the produce the radical cation and dication, respectively, as confirmed by the Vis/Nir and esr spectra. The redox waves are chemically reversible and are well separated (ca. 200 mV) in the cyclic voltammogram and suggest that the same electrochemical behavior should be observed with the next higher oligomers or in the π-conjugated segments of polythiophene. Thus the broad, featureless voltammogram observed with films of polythiophene is not an inherent property of the polymer segments but may reflect complications from the solid state nature of the film.

Dear Sir:

The electro-oxidation reactions of polythiophene films produce complicated cyclic voltammograms. The waves are often broad, deformed and appear at the foot of a large anodic current which often continues to rise until the films are decomposed or 'burned' off of the electrode. There is often a prewave as a shoulder,[1-7] and its visiblity varies with the film thickness, substituents on the polymer[5-7] and electrolyte.[8] A recent electrochemical-ESR study showed that the prewave is associated with the one electron oxidation to produce the polaron state and the main peak corresponds to the formation of bipolarons.[3] In contrast, the electrochemical oxidation of the thiophene dimer, trimer and tetramer (unsubstituted and substituted) in liquid SO_2 at -44 °C and in CH_3CN leads to well-separated anodic processes.[9,10] The electrochemistry of the higher oligomers has not been reported even though there are many recent studies on the chemistry of these compounds.[11-17] In this study, α-α coupled thiophene oligomers with terminal α-$(CH_3)_3Si$ groups (α-TMS) and β-CH_3 groups are used to study the importance of the second oxidation reaction at room temperature as a model study for the polymer segments in the absence of lattice interactions, close counterion effects, capacitance[18] and resistance[19] as may occur in a film.

The soluble α,α coupled thiophene oligomers with the terminal α-TMS groups and β-methyl groups were prepared by Ni- and Pd- catalyzed reactions of the corresponding halide, stannane or Grignard derivatives.[20] The cyclic voltammetry and chronocoulometry of the oligomers (10^{-4} M) in 0.1 M Et_4NBF_4/CH_2Cl_2 solutions were recorded using a 0.5 cm Pt electrode and an SCE double junction electrode, and with a PAR model 273. The electrochemical data are summarized in Table 1. The heptamer VII, pentamer V and tetramer IV all show two one electron redox waves which can be cycled with chemical

reversibility. The peak separations for the second oxidation is slightly higher (70-100 mV) but similar to the separation observed with $FeCp_2$ (E_{pa} = 0.59 V, ΔE = 70 mV). The i_{pa} values scale linearly with the square root of the sweep rate as expected for a diffusion limited reaction. Chronocoulometry for the first reaction showed a linear q vs $t^{1/2}$ dependence. For VII, D is 1.2×10^{-5} cm^2/s, and n is 1.04 for the first oxidation, where n is obtained from a comparison of $nD^{1/2}$ from the slope in the q vs $t^{1/2}$ plot with $n^{3/2}D^{1/2}$ from the slope in the i_{pa} vs $v^{1/2}$ plot. With this same procedure, n equal to 0.99 was obtained with ferrocene. For the second oxidation, n equal to ca. 1 was obtained from the relative slopes in the q vs $t^{1/2}$ plots for steps anodic of the first and the second wave, respectively. Similar values were obtained for V. The ca. 0.2 V separation between the two waves parallels the separation observed with polythiophene films containing alkoxy groups[3,5,6] and with poly(3-methylthiophene) films.[8] The second oxidation is irreversible with the timer III and not visible with the dimer II. Thus four or more thiophene units are required to stabilize the dication at room temperature.

The E_{pa} values for the five oligomers in the Table plot linearly with both 1/(the number of rings) with slope 1.7 and with the band edge in the visible spectrum of the neutral oligomer with slope 0.57. The corresponding slopes for the unsubstituted series are 1.5 and 0.52, respectively.[21] Thus in solution, the methyl groups do not affect the π-conjugation in the monotonically increasing segments as is observed with other substitutents,[22] and, the α-TMS group is known to have a small effect on the redox potential.[23] It is interesting to note that VII and V dications support 0.3 - 0.4 charges/ring, yet the stable oxidation level (average) for the thicker polythiophene films is 0.06 - 0.35 charges/ring.[1,2,8,24-29]

Chemical oxidation [14-16] of VI and VII with 2 moles $FeCl_3$ yields the radical cation as evident by the strong signal in the ESR spectrum with g = 2.004 which almost vanishes upon further oxidation with an additional 2 moles of $FeCl_3$. Therefore, the two oxidation waves observed electrochemically correspond to the sucessive formation of the radical cation and dication. Concurrent with the evolution of the ESR signal is a dramatic change in the Vis/NiR spectra. The absorption at 447 nm for the neutral VII disappears upon oxidation to the radical cation and double peaks appear at 745 and 829 nm and at 1061 and 1782 nm (blue) in line with previous reports.[14-16] The radical cation is stable at room temperature for at least several hours. Further oxidation to the dication changes the absorption spectrum and only peaks at 1074 and 1230 nm are observed. Similar changes are observed in the spectra for the pentamer except that the absorptions are blue shifted. Finally, III can be oxidized to the radical cation which has a stron ESR signal (g = 2.004) and shows two major peaks at 557 and 878 nm in the Vis/NiR spectrum.

In summary, the stepwise oxidation to form the stable radical cation and dication can be accomplished at room temperature with thiophene oligomers containing 4 or more units. The ca. 0.2 V separation between the first and second oxidation suggests that two separate oxidation waves should be visible in the room temperature voltammogram for the next higher oligomers and for the π-conjugated segments of polythiophene. Therefore, the broad, featureless voltammograms observed with the polythiophene films may not be an inherent property of the polymer segments, but instead may reflect the complications caused by the lattice and counter-ion interactions, film resistance[18], capacitance,[19] and irregular couplings in the polymer.[30]

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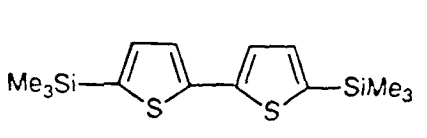
Table 1. Summary of Electrochemical Data.

Oligomer	Epa_1,Epa_2, V	ΔEp, mV	n_1 ,n_1+n_2	E(hν), eV
VII	0.86,1.04	60,80	1.06, 2.05	2.36
V	0.98,1.20	60,70	1.04, 1.98	2.52
IV	1.03,1.35	80,100		2.68
III	1.16,1.53	80	0.95, --	3.04
II	1.46[a]			3.43

[a]Reported Epa values for II and bithiophene are 1.14 and 1.32 V in CH_3CN, respectively.[23]



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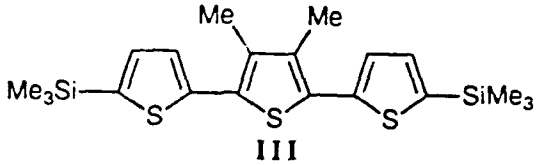

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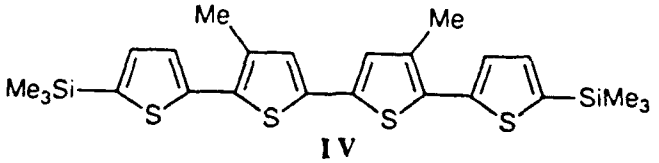

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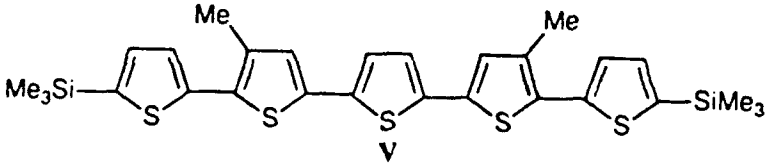

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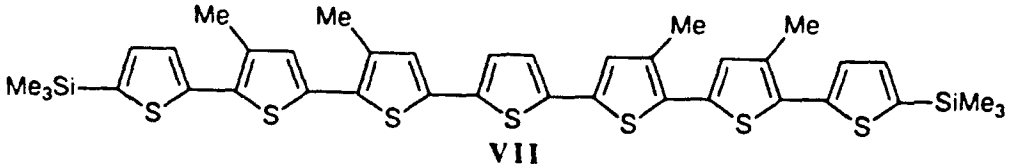

VII

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